Solvay Chemicals

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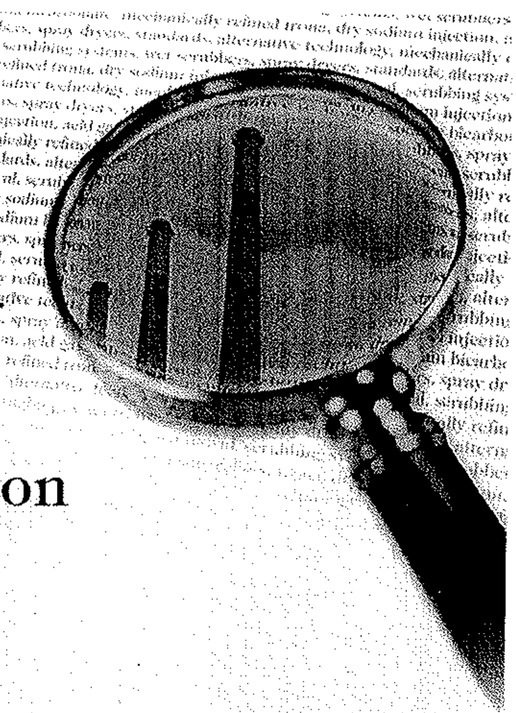


Trona Use In Dry Sodium Injection For Acid Gas Removal

Abstract

In recent years, federal and state regulatory agencies have tightened air emission standards. Two of the acid gases, hydrochloric acid (HCl) and sulfur dioxide (SO_2), are under heavy scrutiny for reduction. Most traditional scrubbing systems, i.e., wet scrubbers and spray dryers, meet the standards, but they typically are high in capital cost, have significant space requirements for equipment, and are difficult to maintain. Dry sodium injection (DSI) is an alternative technology that has been shown to be effective in HCl and SO_2 removal, without the drawbacks of traditional systems.

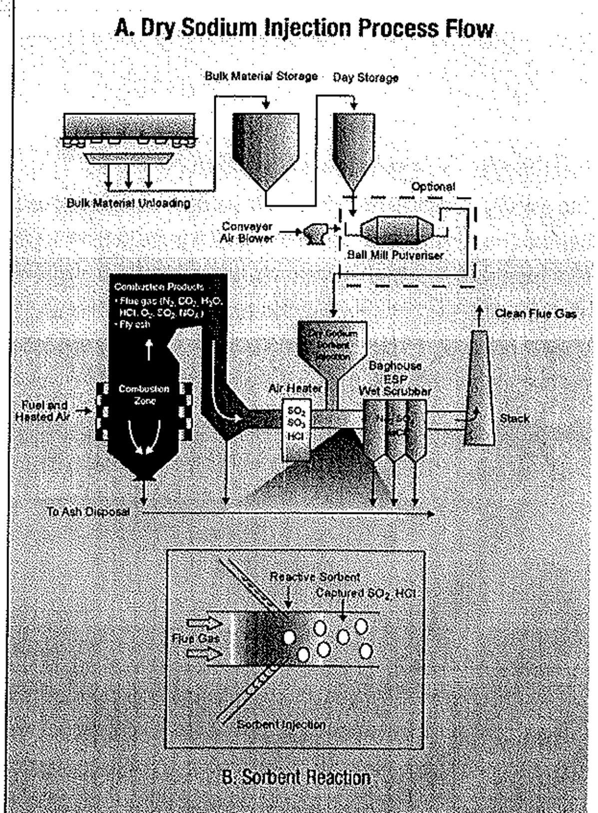
This paper covers the mechanics of dry injection scrubbing using the most effective sorbents, sodium bicarbonate and mechanically refined trona (natural sodium sesquicarbonate).

It presents DSI performance data for Chambers Medical, originally located in Hampton, SC. This facility incinerated local medical and municipal solid waste, and had begun using mechanically refined trona for HCl and SO_2 removal in late 1991. The data presented for mechanically-refined trona covers two products marketed by Solvay Chemicals: T-50® trona, which is coarse grade (~250-300 µms) and T-200® trona which is fine grade (~23 µms).

Dry Sodium Injection

Dry sodium injection is a low cost alternative to a spray dry or wet scrubbing system for the removal of HCl and SO_2. As Figure 1-A illustrates, the process requires no slurry equipment or reactor vessel because the sorbent is stored and injected dry into the flue duct where it reacts with the acid gas. The spent sorbent is collected dry, either through a baghouse or electrostatic precipitator. It also can be collected wet through an existing wet scrubber vessel should DSI be used for trim scrubbing of acid mist.

Figure One: Typical Dry Sodium Injection System



Sodium bicarbonate and sodium sesquicarbonate are the most effective products for use in this application. Both products undergo rapid calcination of contained sodium bicarbonate to sodium carbonate when heated at or above 275°F. The "popcorn-like" decomposition creates a large and reactive surface by bringing unreacted sodium carbonate to the particle surface for HCl and SO_2 neutralization (see Figure 1-B). The byproducts of the reactions are sodium chloride and sodium sulfate, respectively, and are collected with fly ash. Table 1 summarizes the chemical compositions and reactions of both sorbents in acid gas removal.

Table 1. Acid Gas Removal Using Sodium Sorbents

Sodium Sorbent Decomposition	
Sodium Bicarbonate	$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + H_2O + CO_2$
Sodium Sesquicarbonate	$2\,[\,Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O\,] \xrightarrow{\Delta} 3Na_2CO_3 + 5H_2O + CO_2$
Acid Gas Neutralization	
HCl Removal	$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
SO_2 Removal	$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2$ and $Na_2SO_3 + \tfrac{1}{2}O_2 \rightarrow Na_2SO_4$

Sodium Sorbents Reactivity

The amount of sorbent injected into the flue gas is presented on a normalized basis and is referred to as the normalized stoichiometric ratio (NSR). The NSR expresses the stoichiometric amount of sorbent required to react with all of the acid gas. HCl neutralization requires one mole of sodium per one mole of HCl present whereas SO_2 neutralization requires two moles of sodium per one mole of SO_2 present. On a molar basis this relation is:

$$NSR = \frac{\left[\dfrac{\text{(moles of sodium injected)}}{\text{(moles of acid gas entering system)}}\right]}{\left[\dfrac{\text{moles of sodium theoretically needed}}{\text{to react with a mole of acid gas}}\right]}$$

Or on a mass basis:

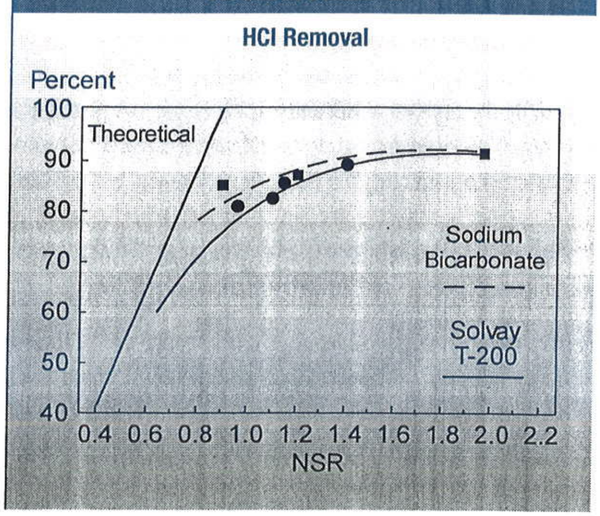
$$NSR = \frac{\left[\dfrac{\text{(mass of sodium injected)}}{\text{(mass of acid gas entering system)}}\right]}{\left[\dfrac{\text{mass of sodium theoretically needed}}{\text{to react with a unit mass of acid gas}}\right]}$$

The sorbent utilization rate (U) is the fraction of the injected sorbent that reacts with the acid gas. It is expressed as:

$$U(\%) = 100 \times \frac{\text{Fraction of Acid Gas Removal}}{\text{NSR}}$$

The Central Study and Research Center (CER) of Solvay S.A. located in Dombasle, France has a pilot micro-injection unit for DSI testing of sorbents. In 1993, they conducted pilot-scale tests using sodium bicarbonate and T-200 trona (natural sodium sesquicarbonate) to compare HCl and SO_2 removal rates on an NSR basis. The results are highlighted in Figure 2 for HCl removal and Figure 3 for SO_2 removal.

Figure 2. CER Pilot Micro-Injection Test/HCl Removal



Stoichiometrically, Solvay Chemicals T-200 trona should yield greater neutralization of both acid gases than sodium bicarbonate due to the higher percent of contained sodium carbonate. However, actual lab tests and field applications reveal contrary performance data. Both sorbents essentially are equal in HCl removal. In contrast, sodium bicarbonate has a removal efficiency of up to 33% over the performance of T-200 trona when SO_2 removal is less than or equal to 90%. Enhanced DSI performance results with sodium bicarbonate, especially in the case of SO_2, are attributed to greater carbon dioxide (CO_2) liberation during calcination.The phenomenon is thought to further augment surface area, thus exposing more sodium carbonate for reaction.

According to the pilot work performed by Solvay S.A.'s CER group in July 1993, sodium bicarbonate and T-200 trona achieved 90% HCl removal at a 2.0 NSR. T-200 was further tested in three separate municipal solid waste facilities for HCl removal. The test results showed the product achieved greater than 95% HCl removal at a 1.0 NSR. Although sodium bicarbonate wasn't tested, previous testing and field experience indicate similar results would have been achieved.

It is evident by examining Figure 3 that the utilization rate of both sorbents declines dramatically when SO_2 removal surpasses 90%. This occurrence is well documented in field applications. It stresses the point that DSI is not an efficient technology in medium-to-high sulfur abatement applications.

Nitrous oxide (NO_x) removal ranging between 10-20% also occurs during SO_2 abatement in DSI. The actual amount of NO_x removed is directly related to the amount of SO_2 removed. Figure 3 highlights the percent of NO_x removed in tandem with SO_2 in the CER tests.

A plant's operating conditions will ultimately affect the performance of the sodium bicarbonate and sodium sesquicarbonate in acid gas removal. The most important variables for high removal efficiency are injection temperature (325-601°F), H_2O concentration (=5%), fine particle size (-20 µms), and retention time where acid gas is in contact with the sorbent.

Solvay Chemicals T-50 trona and T-200 trona are the most cost-effective sorbents in DSI applications, even taking into consideration the enhanced removal efficiency of sodium bicarbonate in SO_2 removal. These products cost significantly less than sodium bicarbonate, especially if finer grades are purchased as a means to eliminate on-site milling.

The following case study illustrates the ease of retrofitting DSI into an operation. It also shows the effect operating parameters have upon the ultimate effectiveness of the sorbent.

Figure 3. CER Pilot Micro-Injection Test/SO_2 and NO_x Removal

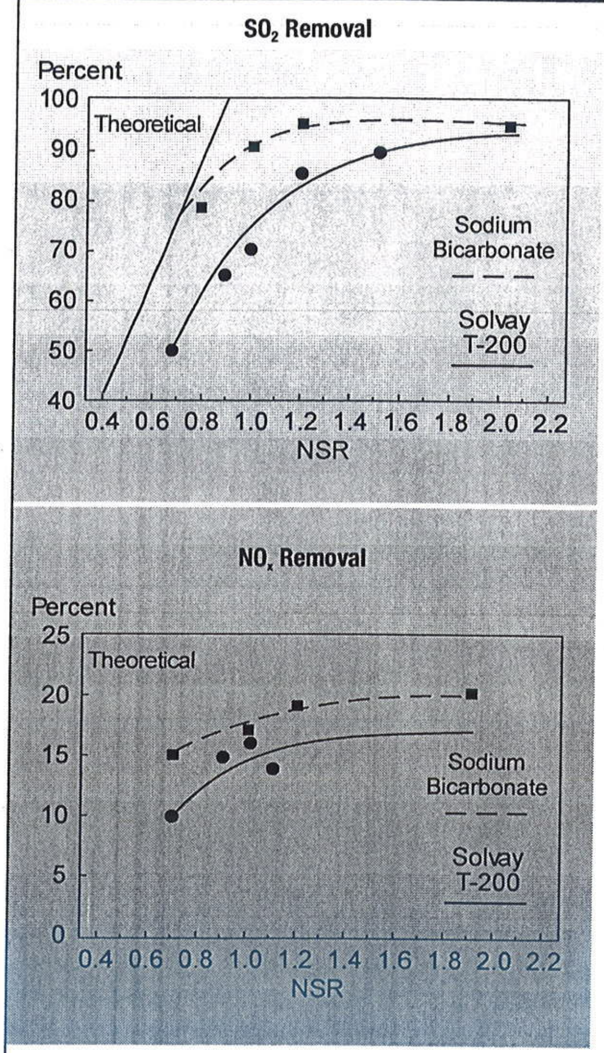


Table 2. Chambers Medical Air Emission Test Results (May 1992)

Test A - Medical & MSW

HCl Removal

Inlet

Test No.	PPMdv A	PPMdv B	PPMdv Avg.	PPMdv Outlet	% Removal
M26-R2A	150	151	150	7.1	95.3
-R3A	207	283	245	11.5	95.3
-R4A	226	215	220	9.8	95.5
Average	194	216	205	9.5	95.4

SO_2 Removal Inlet

Test No.	PPMdv A	PPMdv B	PPMdv Avg.	PPMdv Outlet	% Removal
M6C-R1B	109	33	71	20.9	70.6
-R2B	97	38	67	23.3	65.3
-R4B	149	43	96	28.9	69.9
Average	119	38	78	24.4	68.7

Test B - Tires & Medical Waste

HCl Removal

Inlet

Test No.	PPMdv A	PPMdv B	PPMdv Avg.	PPMdv Outlet	% Removal
M26-RIB	281	269	275	20.8	92.4
-R2B	223	158	191	10.5	94.5
-R3B	283	249	266	11.0	95.9
Average	262	225	244	14.0	94.3

SO_2 Removal

Inlet

Test No.	PPMdv A	PPMdv B	PPMdv Avg.	PPMdv Outlet	% Removal
M6C-RIB	88	73	80	23.2	71.0
-R2B	149	123	136	33.0	75.7
-R4B	127	66	96	24.1	74.9
Average	121	87	104	26.8	74.3

Case Study - Chambers Medical

In 1989, Chambers Medical, originally of Hampton, SC, operated three incinerators that were fired with medical and municipal solid waste. Two 20,000-pound-per-hour boilers were followed by economizers.

This facility had a waste burn capacity of 200 tons per day. Typical waste composition averages were 35% medical waste and 65% municipal solid waste.

In early 1989, Chambers retrofitted the facility to add dry sodium injection for HCl removal. The project included the addition of a reaction chamber (serpentine duct configuration) to allow a retention time of three seconds for sorbent-to-gas contact. A hopper-to-mill unit was added to the discharge to pulverize sorbent before injection. The facility had a two-field electrostatic precipitator on site for particulate collection. Figure 4 (see page 6) is a DSI process flow diagram for Chambers.

Chambers started the DSI unit using sodium bicarbonate. It achieved an average HCl removal rate of 98% or 10 PPMdv exit the stack.This rate far surpassed the state's emission standard of 83% removal or 100 PPMdv exit the stack. In subsequent years, Chambers' state emission regulation for HCl tightened to 90% removal or 30 PPMdv at the stack, whichever provided the highest removal rate. SO_2 emissions had never been regulated by the state. However, Chambers had periodically included SO_2 in its HCl compliance test to verify the level.

In late 1991, Chambers tried Solvay Chemicals' T-200 trona as a means to save on sorbent cost. They found the particle sizing of the product was too fine to handle through the existing hopper-to-mill unit. This situation led Chambers to temporarily use the coarser grade of mechanically-refined trona product that Solvay Chemicals offers under the name of T-50 trona. This product has a mean particle size range of 250-300 μms before pulverization.

Chambers performed an air emission test in May 1992. It used Solvay Chemicals' T-50 trona as the sorbent, which had a mean particle average size of 35 μms after milling. The sorbent injection rate was 272 kilograms per hour and the duct injection temperature was 302-316°C. Chambers documented both HCl and SO_2 removal rates. The emission tests were performed for two different waste streams: Test A) medical & municipal solid waste; and Test B) tires and medical waste.

Table 3. Chambers Medical Air Emission Test Results (September 1994)

Test C - Medical & MSW

HCl Removal

Inlet

Test No.	PPMdv A	PPMdv PPMdv B	PPMdv Avg.	Outlet	% Removal
M26-RIA	285	258	271	3	98.9
-R2	337	235	286	1	99.6
-R3	258	226	242	1	99.6
Average	293	240	266	2	99.3

SO_2 Removal

Inlet

Test No.	PPMdv A	PPMdv PPMdv B	PPMdv Avg.	Outlet	% Removal
		NOT PERFORMED			

Table 2 presents the HCl and SO_2 removal results for the two waste streams (Tests A and B). Removal rates could not be expressed in terms of NSR due to the combined removal of HCl and SO_2. As an alternative, removal rates were calculated by material balance (gas outlet versus gas inlet rates). The results show Chambers achieved an average HCl removal rate of 95% or 12 PPMdv at the stack. Simultaneously, Chambers also averaged over 71% SO_2 removal or around 4 PPMdv exit the stack.

In early 1993, Chambers completed the modifications to handle T-200 trona through the hopper-to-mill system. It performed an air emission test in September 1994. This test solely documented HCl removal using unpulverized T-200 trona at 23 µms, but the sorbent injection rate was reduced from 272 to 204 kilograms per hour. The waste stream makeup was medical and municipal solid waste, the same as Test A in Table 2.

Table 3 details the performance results of Solvay Chemicals' T-200 trona. The test results indicate Chambers achieved greater than 99% in HCl removal even though the HCl concentration was higher than in Tests A and B and sorbent injection was reduced by 25%. It can be assumed SO_2 was present even though it was not documented. SO_2 removal should have been greater than 70%. Chambers concluded the performance improvement came from the finer particle size of the T-200 trona product. After the trial, Chambers eliminated milling and received state approval to use the lower T-200 trona injection rate of 204 kilograms per hour.

Summary

DSI is a simple technology that is easily added into an operation. Many lab, pilot and plant applications have shown sodium bicarbonate and natural sodium sesquicarbonate are the most effective sorbents for acid gas removal, whether the gases are neutralized together or independently. Solvay Chemicals markets mechanically-refined trona under the trade names of T-50 trona (coarse grade) and T-200 trona (fine grade). As Chambers demonstrated, both grades will perform adequately in DSI for acid gas removal. Solvay Chemicals' T-200 trona is the choice product because of its fine particle size. Chambers achieved greater than 99% HCl removal using T-200 trona.

Regardless of the product grade and the greater efficiency of sodium bicarbonate in SO_2 removal, the cost effectiveness of Solvay Chemicals' T-50 trona and T-200 trona products positions them as the lowest cost sorbent to companies utilizing DSI.

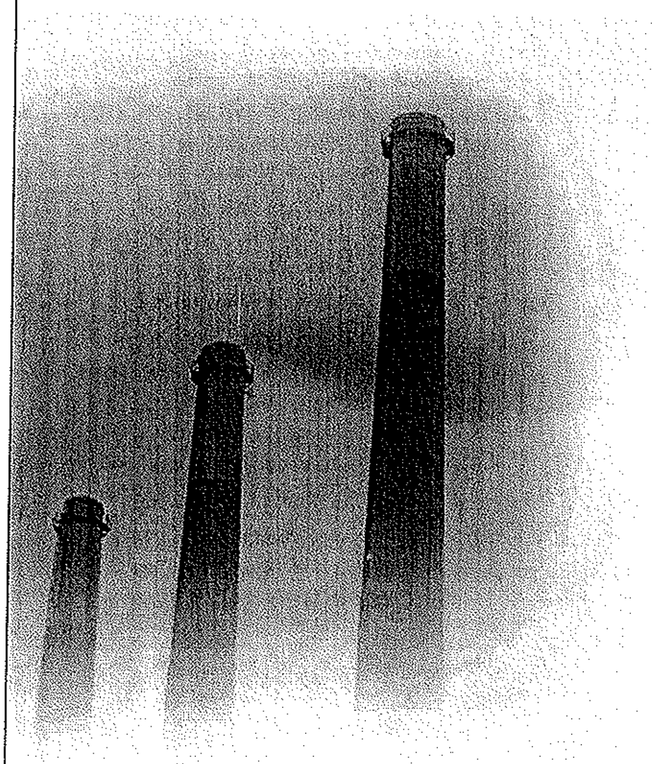


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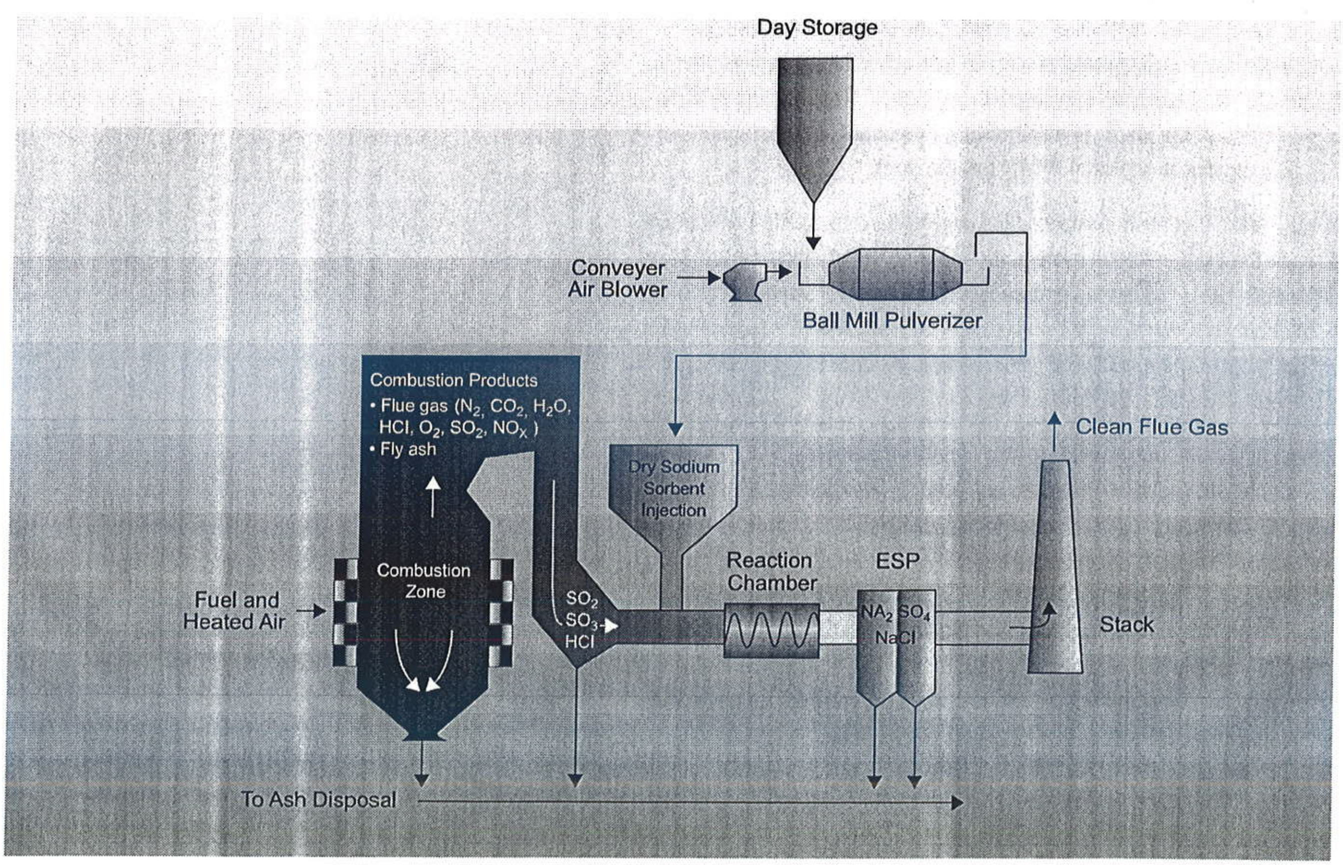
Figure 4. Chambers Medical - Dry Sodium Injection Process Flow



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